Fabrication of Nanostructured Heterojunction LEDs Using Self-Forming "Moth-Eye" Type Arrays of n-ZnO Nanocones Grown on p-Si (111) Substrates by Pulsed Laser Deposition

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ABSTRACT

ZnO nanostructures were grown on Si (111) substrates using Pulsed Laser Deposition. The impact of growth temperature (Ts) and Ar pressure (P_{Ar}) on the morphology, crystal structure and photoluminescence was investigated. Various types of ZnO nanostructures were obtained. Self-forming arrays of vertically-aligned nanorods and nanocones with strong c-axis crystallographic orientation and good optical response were obtained at higher Ts. The nanocone, or "moth-eye" type structures were selected for LED development because of their graded effective refractive index, which could facilitate improved light extraction at the LED/air interface. Such moth-eye arrays were grown on p-type Si (111) substrates to form heterojunction LEDs with the n-type ZnO nanocones acting as an active component of the device. These nanostructured LEDs gave rectifying I/V characteristics with a threshold voltage of about 6V and a blueish-white electroluminescence, which was clearly visible to the naked eye.

Keywords: Nanostructures, n-ZnO/p-Si, heterojunction Light Emitting Diode

1. INTRODUCTION

ZnO is a remarkable multifunctional material with a distinctive set of properties including a direct bandgap of ~3.4eV and an exciton binding energy of ~60meV. It also has a high transparency over the visible spectrum, a strong piezoelectric response, a very wide range of tuneable conductivities (varying from semi-insulating to semi-metallic) and good bio-compatibility. As a result, ZnO has many established and emerging applications spanning from use as an ultra-violet filter in sun cream to varistor, light emitting diode (LED) [1] and surface acoustic wave applications [2]. ZnO also exhibits one of the largest families of nanostructures of all materials systems with a huge range of potential applications opening up as a result of the nanostructuring. Indeed, ZnO nanowires were recently identified by Thomson-Reuters as the most researched nanomaterial in 2008 [3].

In previous work [4,5] it was established that Pulsed Laser Deposition (PLD) gave nanostructures with superior crystallinity compared with those prepared using Metal Organic Chemical Vapor Deposition or Physical Vapour Transport. This paper compares the forms and properties of ZnO nanostructures prepared using PLD on Si (111) substrates under various growth conditions. The paper then considers the optimum structure for LED light extraction and describes the fabrication of heterojunction LEDs employing n-type ZnO nanostructures as active components [6,7].

2. EXPERIMENT

ZnO nanostructures were grown by PLD from a 99.99% pure sintered ZnO target using a KrF excimer laser (248 nm) at a frequency of 10 Hz. The vacuum chamber was evacuated using a turbo-molecular pump to a pressure of about 1×10^{-6} Torr. The impact of growth conditions was investigated as a function of both Ar partial pressure (P_{Ar}) and growth temperature (Ts). Si (111) was chosen as the substrate and growths were all made for a duration of about 10 minutes. Sample morphology was studied using a Hitachi S4800 Field Emission-Scanning Electron Microscope (FE-SEM). The crystal quality of the nanostructures was investigated using X-Ray Diffraction (XRD) performed in a Panalytical MRD

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Pro system using Cu Ka radiation. Optical properties were studied via Room Temperature (RT) PhotoLuminescence (PL) with a continuous-wave, frequency-doubled, argon-ion laser (244 nm, power of 30mW). Heterojunction LEDs were made by growing n-type ZnO nanostructures on p-type Si (111) substrates. Device I/V characteristics and electroluminescence (EL) were investigated using a Karl-Suss probe station, a Keithley 2400 Source-Meter and an Olympus digital camera.

3. RESULTS & DISCUSSION

3.1 The Dependence of the Nanostructures on Growth Conditions

Figure 1 shows SEM images of samples obtained under various growth conditions. The lower and intermediate Ts gave films with a relatively high surface roughness but no distinct nanostructures. Samples grown at higher Ts showed dense arrays of vertically-aligned nanostructures. Growths at higher P_{Ar} gave nanorods about 200 nm in diameter and 3 microns in length, which were rounded at the tips. Samples grown at lower P_{Ar} gave a "moth-eye" type array of nanocones [8,9], which were about 3 microns in length and 200 nm in diameter at the base.

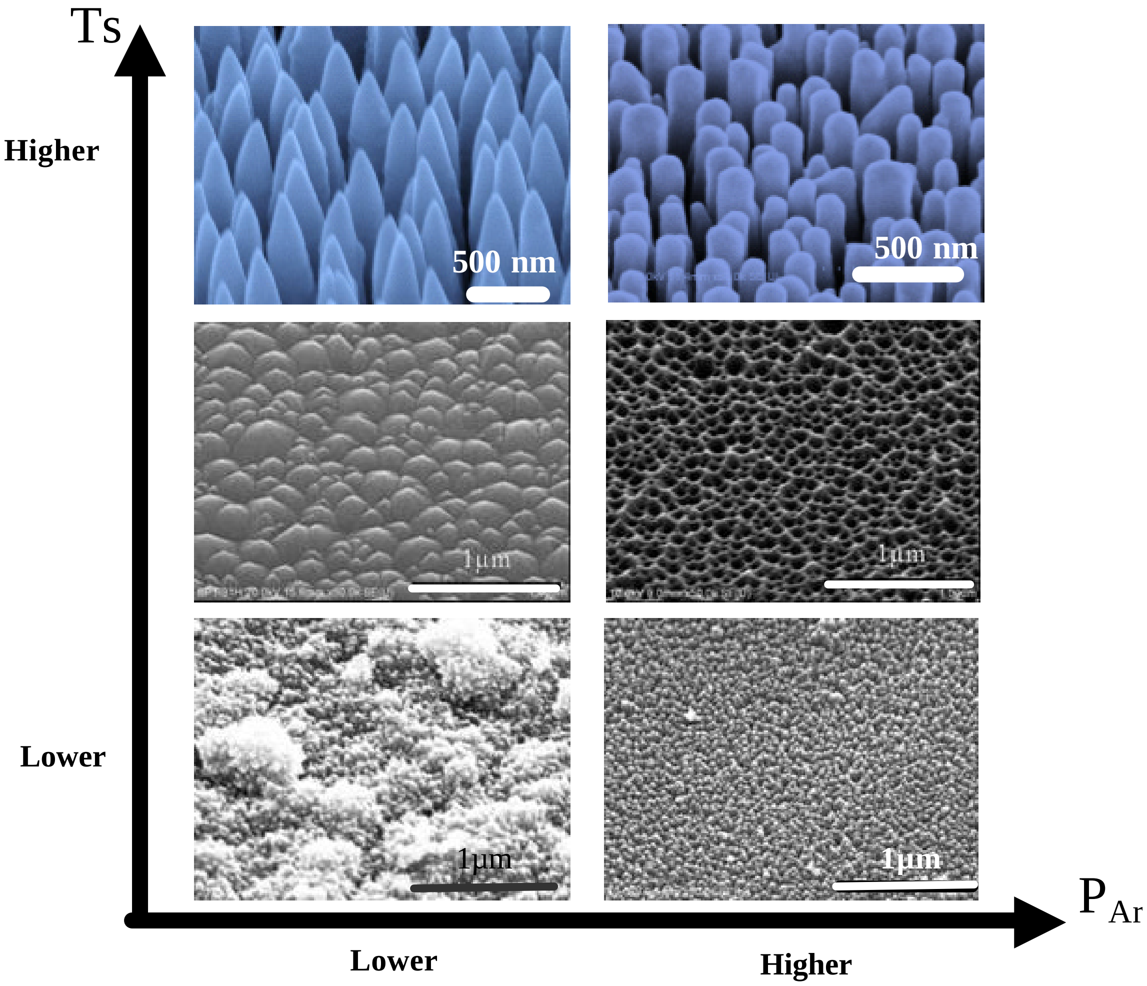

Figure 1: SEM images of ZnO nanostructures grown by PLD on Si (111) from low to high P_{Ar} / Ts.

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Figure 2 shows the XRD scans for the (0002) peaks of the nanostructures grown at higher Ts. The main peak position in the $2\theta/\Omega$ scans is similar for both samples, corresponding to c lattice parameters of 5.205 and 5.206 Å for the lower and higher P_{Ar} samples, respectively. This is what would be expected for relaxed wurtzite ZnO. Both $2\theta/\Omega$ peaks also show a higher-angle broadening at the base of the $2\theta/\Omega$ peak, indicative of contribution of a region with a smaller c lattice parameter. This could be due to disorder at the start of nanostructure growth creating a less dense a-b plane at the base of the columns/cones (and thus a larger a lattice parameter). The $2\theta/\Omega$ scan for the sample grown at lower P_{Ar} presented a significantly more intense peak than that for the nanostructures grown under higher P_{Ar}. This suggests that the sample grown at lower P_{Ar} was better crystallised. It should be noted, however, that although the samples were analysed using the same XRD configuration, it is difficult to make direct comparison of peak intensity because of possible differences in growth rates. The Full Wave Half Maxima (FWHM) for the two samples were similar at 0.015 and 0.014 for lower and higher P_{Ar}, respectively.

The Ω scan for the sample grown at lower P_{Ar} showed a smaller FWHM than that for the sample grown at higher P_{Ar} (0.64° vs 0.79°). This suggests that the lower P_{Ar} sample was more highly c-axis oriented.

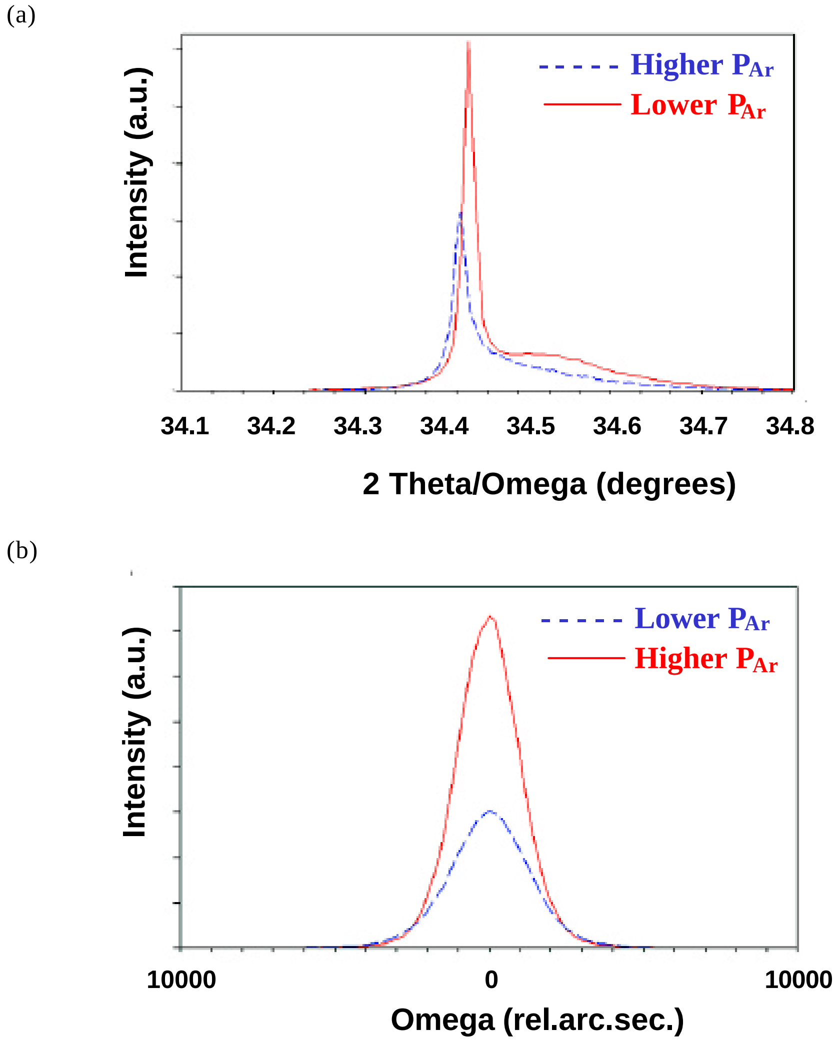

Figure 2 : (a) XRD 2 q/W & (b) W scans for the (0002) peak of the nanostructured ZnO grown on Si (111) at higher Ts as a function of P_{Ar}

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RT PL for the samples grown at higher Ts are shown in Figure 3. The spectra for both P_{Ar} showed low green signals and strong main peaks with FWHM of about 51 nm and main emission wavelengths (λ_{MAX}) of about 390.5 nm, which is typical for Near Band Edge (NBE) emission from wurtzite ZnO. This indicates that the nanostructures had good crystal quality with a relatively low defect density. The spectrum for the nanostructures grown under higher P_{Ar} had a significantly more intense peak than that for the nanostructures grown under lower P_{Ar}. This could indicate that the higher P_{Ar} nanostructures present a better cristallinity. It should be noted, however, that although the spectra were acquired under the same conditions, it is possible that differences in growth rates or other factors (such as beam scattering variations) may invalidate such direct comparison of peak intensity.

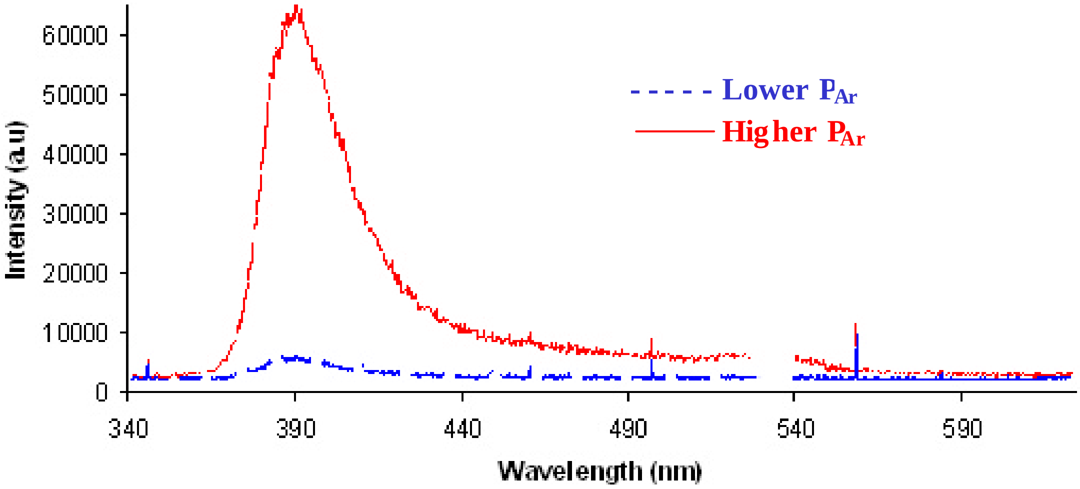

Figure 3: (a) PL spectra of the nanostructured ZnO on Si (111) grown under higher and lower P_{Ar}

3.2 Device Fabrication and Characterisation

The “moth-eye” type nanostructures, grown at lower P_{Ar}, were chosen for use in the LED because they represent a graded effective refractive index (Figure 4) at the LED/air interface, which could promote improved light extraction [10].

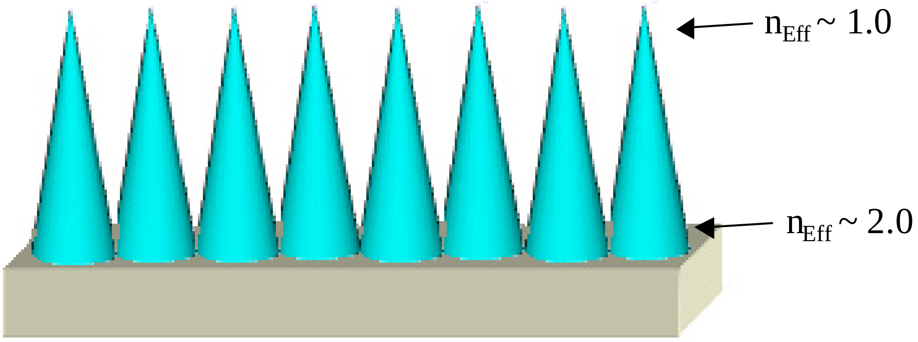

Figure 4: Schematic illustrating the graded effective refractive index of the nanocone type structures

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A schematic of the device structure grown using these nanocones is shown in Figure 5. Metallic contacts were applied to the nanostructures surface and the backside of the substrate.

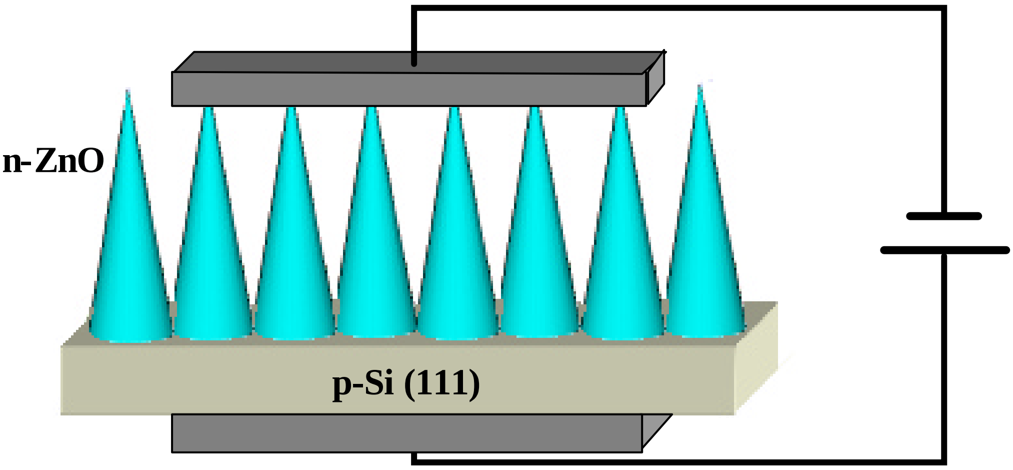
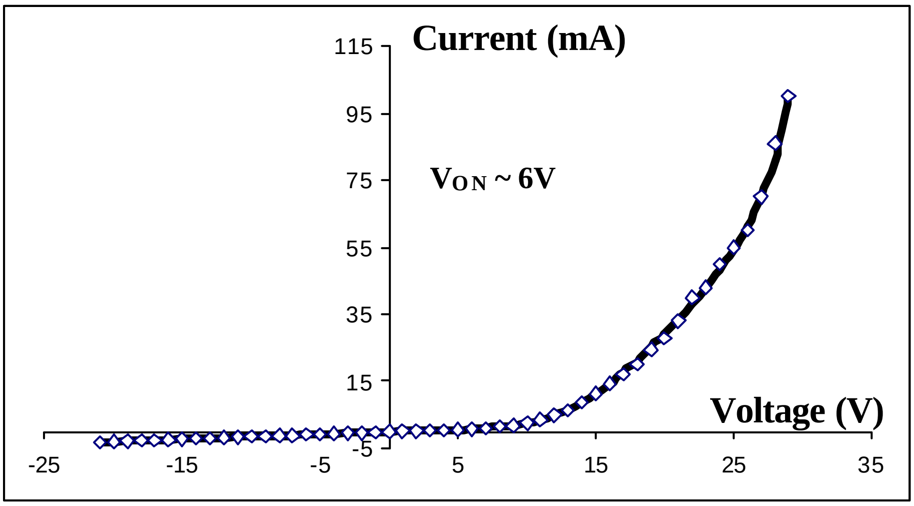


Figure 5: Schematic diagram of the nanostructured n-ZnO/p-Si(111) heterojunction LED.

The I/V characteristics for the device and the contacts are shown in Figure 6.



(a)

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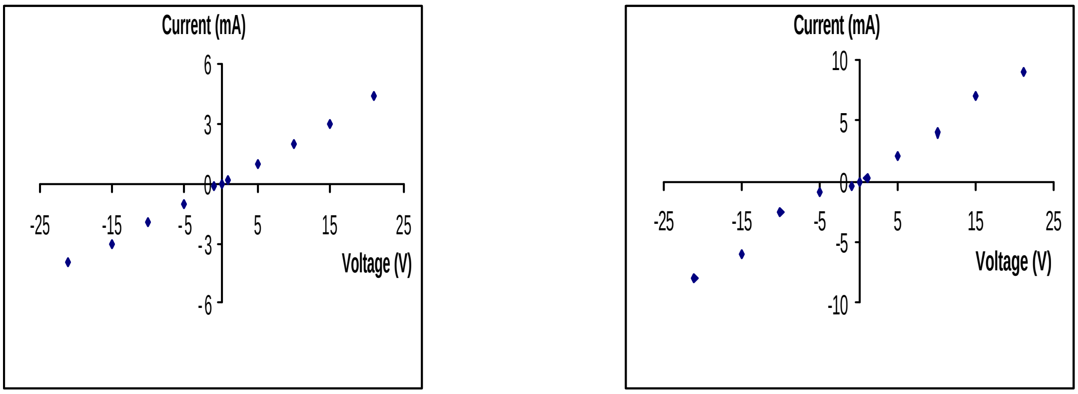


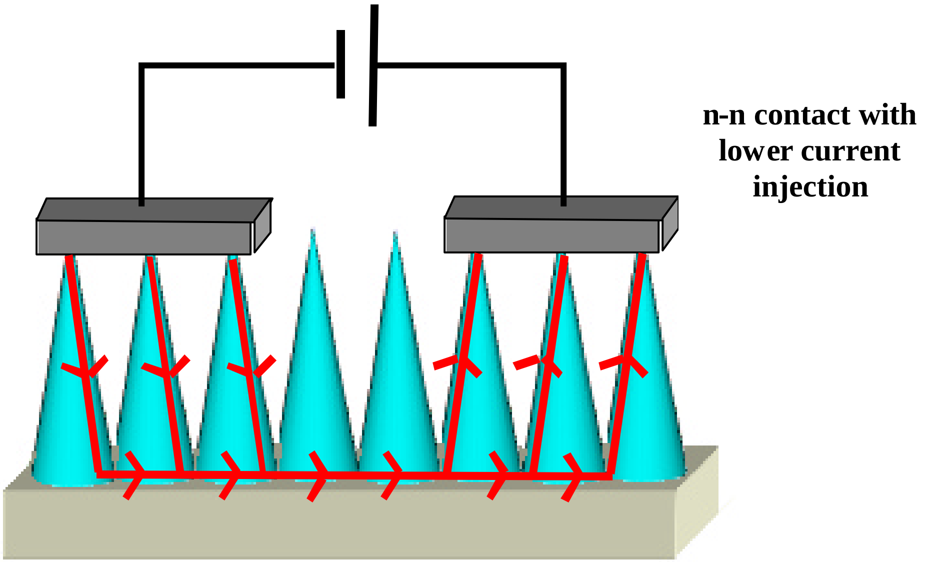
(b)

(c)

Figure 6 (a) I/V characteristic for the n-ZnO nanocone / p-Si (111) heterojunction (b) I/V characteristic for the p-to-p contact, (c) I/V characteristic for the n-to-n contact.

The I-V curves revealed a turn-on voltage of approximately 6V, a series resistance of about 500 ohms and a leakage current of about 2.5 mA at –15V. The I/V characteristic for the p-to-p contact showed very good linearity, indicating that the contacts seemed ohmic, while the I/V characteristic for the n-to-n contact deviated slightly from linearity. This may be due to parallel conduction of the current flow through the p-Si substrate as illustrated in figure 7.

(a)



(b)

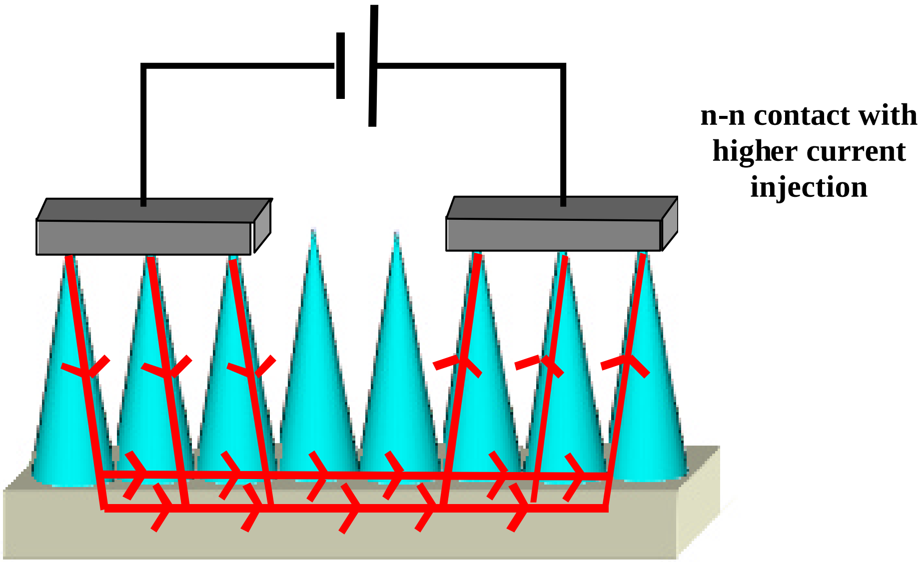


Figure 7: Schematic of the n-to-n contact current flow in the n-ZnO/p-Si LED device with (a) lower and (b) higher current injection.

The device showed a blueish-white EL which was clearly visible to the naked eye for currents over about 25mA. Photographs of the EL are shown in Figure 8. Investigation of the EL spectrum with an integrating sphere is in progress.

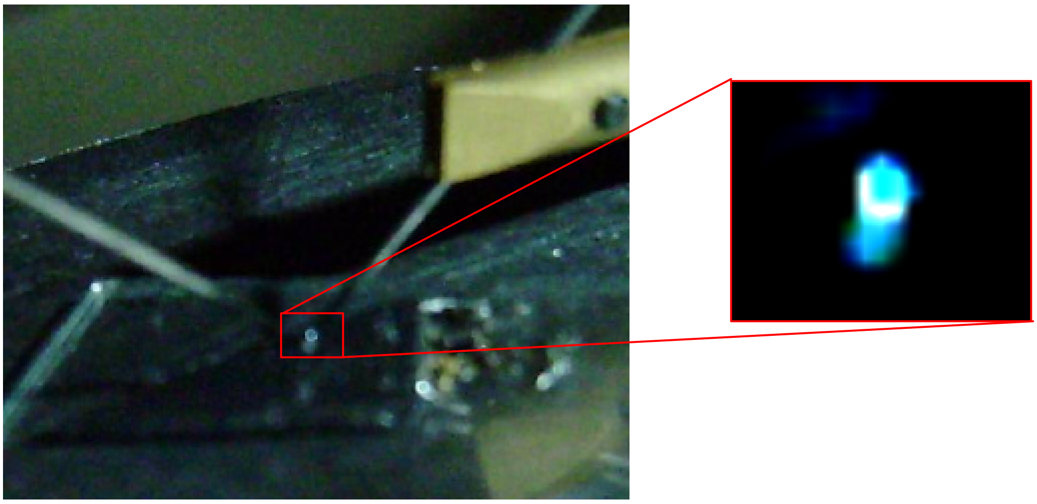


Figure 8: Photographs showing the blueish-white EL emanating from the device for a forward current of about 50mA.

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6. CONCLUSIONS

Nanostructures were grown on Si (111) substrates using catalyst-free PLD. The impact of Ts and P_{Ar} on the sample morphology and properties was investigated. Self-forming, vertically-aligned nanostructures were obtained for growths at higher Ts. Growths at higher P_{Ar} gave arrays of nanorods, while those at lower P_{Ar} gave "moth-eye" type arrays of nanocones. XRD and RT PL studies indicated that the nanostrucutures grown at higher Ts were highly c-axis oriented wurtzite ZnO with strong NBE emission and relatively low defect density. The moth-eye nanostructures were chosen for LED fabrication because of their graded effective refractive index, which may improve light extraction. Heterojunction LEDs were fabricated by growing n-ZnO nanocones on p-Si (111). The devices showed rectifying I/V characteristics and blueish-white EL, which was clearly visible to the naked eye. .

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